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DISPERSED-METAL-TOUGHENED ALUMINA*

T. N. Tiegs and A. J. Moorhead

ABSTRACT

Hot-pressed alumina with a fine dispersion of Cr metal particles showed good fracture toughness ($K_{IC} < 8 \text{ MPa}\cdot\text{m}^{1/2}$) and thermal shock resistance. However, the fracture strengths of these materials were relatively low (190 to 240 MPa vs 350 to 580 MPa for pure alumina). The good fracture toughness and thermal shock resistance were found to be related to the relatively large-grain duplex microstructure of the hot-pressed materials. The fracture toughness of alumina with dispersions of Ni and Pt was found to be inferior to that of the Al_2O_3 -Cr materials. Hot-pressed solid solutions of Al_2O_3 - Cr_2O_3 also showed good fracture toughness ($K_{IC} = 7.3 \text{ to } 7.7 \text{ MPa}\cdot\text{m}^{1/2}$), which was again due to the development of a relatively large-grain duplex microstructure.

INTRODUCTION

Dispersed-metal-toughened (DMT) alumina was originally developed for thermal-shock-resistant insulators to be used in instrument sensors in out-of-reactor safety experiments simulating the reflood phase of a loss-of-coolant accident.^{1,2} During a loss-of-coolant accident the temperature of the reactor core components rises and the components are then subjected to severe thermal shock (on the order of 300°C/s) during reflood. The DMT alumina was developed after it was determined that no commercially available insulator would meet the criteria of low permeability to fluids, high electrical resistance, high thermal shock resistance, and joinability to metals. Our work has involved dispersions of Cr, Pt, and Ni metal particles in an aluminum oxide (Al_2O_3) matrix. Another previous study had used dispersed Mo particles in an aluminum oxide matrix.³

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These previous studies determined that the hot-pressed Al_2O_3 -1 vol % Pt and Al_2O_3 -1 vol % Cr composites had relatively high fracture toughness ($K_{Ic} < 8 \text{ MPa}\cdot\text{m}^{1/2}$), were highly resistant to repetitive thermal transients, and were readily joinable by brazing to metal components. The higher fracture toughness of the chromium-containing material was attributed to superior bonding between the chromium and alumina (possibly due to a chromia layer on the chromium particles) and/or to the rod- or disc-like morphology of the Cr particles (as compared with the more spherical Pt particles).

Recent interest in DMT alumina was for the purpose of determining if the material had applications in advanced heat engine components.^{4,5} The NASA Lewis Research Center (LeRC) had been assigned project management responsibility for the Heavy Duty Transport Technology Project by the Department of Energy. The major thrust of this program was to support long-term, high-risk (but potentially high-payoff) research and development on promising conservation technologies that were related to the heavy-duty transport sector but that were unlikely to be undertaken by the private sector alone. To that end, LeRC issued an Applications Notice describing the areas of interest and invited unsolicited proposals in those areas. Oak Ridge National Laboratory submitted a proposal, which was accepted by LeRC. This report describes the activities performed under that contract.

FABRICATION OF DMT ALUMINA SAMPLES

Fabrication of the DMT alumina composites has been described in detail previously.^{1,2,4} Basically it consists of forming a slurry of alumina powder with a soluble metal precursor compound, reducing the precursor to the base metal at elevated temperature and then hot pressing to form a fully dense piece. Samples with 1 to 8 vol % Cr, 5 vol % Pt and 1 vol % Ni were prepared in that manner. The metal precursors used were chromium nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], platinum chloride (H_2PtCl_6), and nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], respectively. Other pertinent fabrication parameters for the DMT aluminas are given in Table 1.

Table 1. Fabrication parameters for dispersed-metal-toughened alumina

Sample identification	Metal content (vol %)	Type alumina ^a	Powder heat treatment		Hot-pressing conditions		Density		Average grain size (μm)
			Reduction temperature (°C)	Paraffin used	Pressure (MPa)	Temperature (°C)	(Mg/m ³)	(% TD)	
AC-4	8 Cr	A-17	1350	No	55	1610	3.9500	93.2	6.5
AC-5	2 Cr	A-17	1350	No	55	1610	3.8900	96.2	7.5
AC-11	1 Cr	A-17	1150	Yes	41	1610	3.9977	99.6	15
AC-12	2 Cr	A-17	1150	Yes	41	1610	4.0269	99.6	14
AC-13	4 Cr	A-17	1150	Yes	41	1610	4.0730	99.1	10
AC-14	8 Cr	A-17	1150	Yes	41	1610	4.1397	97.7	10
DMT-4	2 Cr	CR-10, A-17	1250	Yes	21	1610	4.000	98.9	5.7
DMT-5	2 Cr	CR-10	1250	Yes	21	1600	3.9953	98.8	5.5
AN-1	1 Ni	A-17	400	No	41	1600	3.990	98.8	5.2
AP-1	5 Pt	A-17	850	No		1600		99.3	N.D.
DMT-9	0	A-17			55	1610	3.9/15	99.8	6.4

^aAlcoa A-17 or Baikowski CR-10.

During the production of these composite insulators, paraffin (as a carbon source) was used with the Al_2O_3 -Cr materials to aid in the reduction of Cr_2O_3 to metallic Cr. (The nickel nitrate and platinum chloride require no carbon for reduction to the base metal.) The initial reports^{1,2,4} indicated no evidence of detrimental effects from any residual carbon. However, analytical chemical analysis of an archive sample from our earlier work revealed substantial amounts of residual carbon (Table 2). Because any free carbon would degrade the properties of the alumina, it was desirable to find ways to reduce or eliminate it.

Thermodynamic calculations indicated that Cr_2O_3 could be reduced to metallic Cr at temperatures $>1100^\circ\text{C}$ in dry hydrogen. Powders were fired at 1200, 1300, and 1350°C (AC-3, AC-2, and AC-4, respectively) under dry hydrogen for 15 minutes. Visual examination of the powders showed that all were pink in color, indicating that a solid solution of Al_2O_3 and Cr_2O_3 had formed. Closer examination of the powder fired at 1350°C (AC-4) showed that indeed some metallic particles had been formed, although an accurate interpretation was difficult because it also had the highest Cr content. However, X-ray diffraction examination of the same powder revealed no metallic Cr (evidently the amount was below the detection limit), but the Al_2O_3 - Cr_2O_3 solid solution was detected. Thus, while some reduction of the Cr_2O_3 to metallic Cr does occur in dry hydrogen at temperatures $>1300^\circ\text{C}$, the kinetics of the reduction are slow enough that most of the Cr_2O_3 appears to go into solid solution with the Al_2O_3 .

Table 2. Summary of results on alternate methods of reduction of Cr_2O_3

Sample identifi- cation	Powder heat treatment ($^{\circ}\text{C}$)	Carbon			Color
		Source	Ratio quantity used ^a	Residual content (ppm)	
Pwd. 8-3-82 ^b	1100	Paraffin	0.306	1767	Black
AC-2	1300	None	0	c	Pink
AC-3	1200	None	0	c	Pink
AC-4	1350	None	0	c	Pink
AC-8	1350	Paraffin	0.306	c	Pink
AC-9	1350	Paraffin	0.306	c	Pink
AC-11	1150	Paraffin	0.306	720	Gray
ACC-7	1350	Carbon black	0.045	173	Pink
ACC-3	1350	Carbon black	0.071	c	Gray

^aIn carbon/ $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Theoretically, reduction of the Cr_2O_3 from 1 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to metallic Cr would require 0.045 g of carbon.

^bArchive powder sample.

^cNot determined.

Using paraffin as the carbon source and firing at 1350°C in dry hydrogen (samples AC-8 and AC-9) also resulted in powders with a distinctive pink color indicative of the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution. Samples fired at 1150°C and using paraffin (AC-11) did not have a pink color but were gray, indicating that some excess carbon was present. Indeed, residual carbon was found by analytical chemistry, but at a lower level than the archive sample fired 50°C lower. This carbon level (~ 720 ppm or 0.07 at. %) was considered to be acceptable.

Carbon black was examined as an alternative to paraffin for the reduction of the Cr_2O_3 (sample ACC-7) with the thought that the amount of carbon could be better controlled by using that carbon source. Although reduction occurred, as evidenced by the visual observation of metallic particles, large residual carbon particulates ($>100 \mu\text{m}$) were observed dispersed throughout the reacted powder. The starting particulate size for the carbon black was on the order of $0.1 \mu\text{m}$, so the cause of such large agglomerates is unknown.

FABRICATION OF ALUMINA-CHROMIA SAMPLES

Samples of the Al_2O_3 - Cr_2O_3 solid solution were also fabricated by hot pressing as shown in Table 3. Our original interest in these samples was to study the long-term oxidation behavior of the metallic Cr, which goes into solid solution with the Al_2O_3 at elevated temperatures. This solid solution is also of interest because of the lower thermal conductivity compared with that of pure Al_2O_3 (ref. 6) (an advantage in uncooled diesel component applications) and also because of the possible strength increase from solid solution hardening of Al_2O_3 by Cr_2O_3 (ref. 7).

Table 3. Fabrication parameters for Al_2O_3 - Cr_2O_3

Sample identification	Composition	Type alumina ^a	Powder heat treatment		Hot-pressing conditions		Density (Mg/m^3)	Average grain size (μm)
			Reduction temperature ($^{\circ}\text{C}$)	Atmosphere	Pressure (MPa)	Temperature ($^{\circ}\text{C}$)		
AC-1	Al_2O_3 -4 wt % Cr_2O_3	A-17			55	1610	3.9000	10
AC-2	Al_2O_3 -8 wt % Cr_2O_3	A-17	1300	H_2	55	1610	3.9370	12
AC-3	Al_2O_3 -16 wt % Cr_2O_3	A-17	1200	H_2	55	1610	3.9500	11
DMT-6 ^b	Al_2O_3 -4 wt % Cr_2O_3	CR-10	1150	Ar	21	1600	4.0253	3.1

^aAlcoa A-17 or Baikowski CR-10.

^bUsed 0.5 wt % MgO .

MICROSTRUCTURE

The metal particles produced by the fabrication route just described are small (0.1 to 2 μm diam) and randomly dispersed throughout the material. They are located at grain boundaries (Fig. 1) and also within the larger grains (Fig. 2). The latter are engulfed when grain growth occurs during hot pressing resulting in the grain boundaries sweeping past the metal particles.

The microstructures of the alumina in these materials can vary significantly. Variables that influence the grain size include the type of Al_2O_3 starting powder, powder treatment, hot pressing conditions, and metal content.

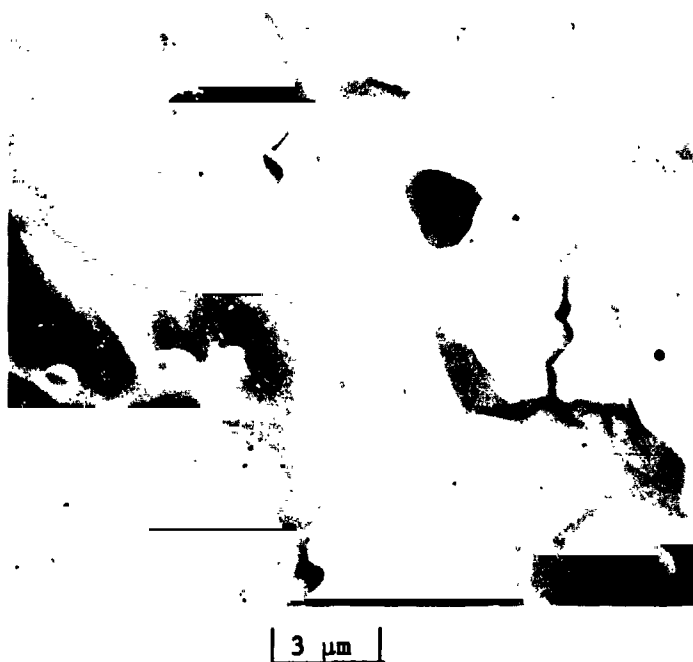


Fig. 1. Fracture surface of hot-pressed Al₂O₃-Cr material showing dispersed metal particles on grain boundaries.

Samples of Al₂O₃-Cr made with Alcoa A-17 alumina and pressed at >41 Mpa and ~1600°C have a relatively large-grain duplex structure shown in Fig. 2. The Al₂O₃-Cr₂O₃ solid solution specimens with similar fabrication parameters had similar microstructures. The Alcoa A-17 has an initial particle size of ~5 μm, but during hot pressing excessive grain growth can occur resulting in the duplex grain structure. As will be discussed later, this duplex structure contributes significantly to the fracture toughness of these materials.

When a finer-grained Al₂O₃ is used as the starting powder (i.e., Baikowski CR-10, ~0.2 μm initial particle size) and is hot pressed at a lower pressure (21 MPa), no excessive grain growth occurs and a duplex structure does not result. As shown in Fig. 3, the microstructure is equiaxed with a relatively small grain size. Like the Al₂O₃-Cr materials, the Al₂O₃-Cr₂O₃ solid solution made with the finer grain Al₂O₃ starting material also had a small equiaxed grain structure.

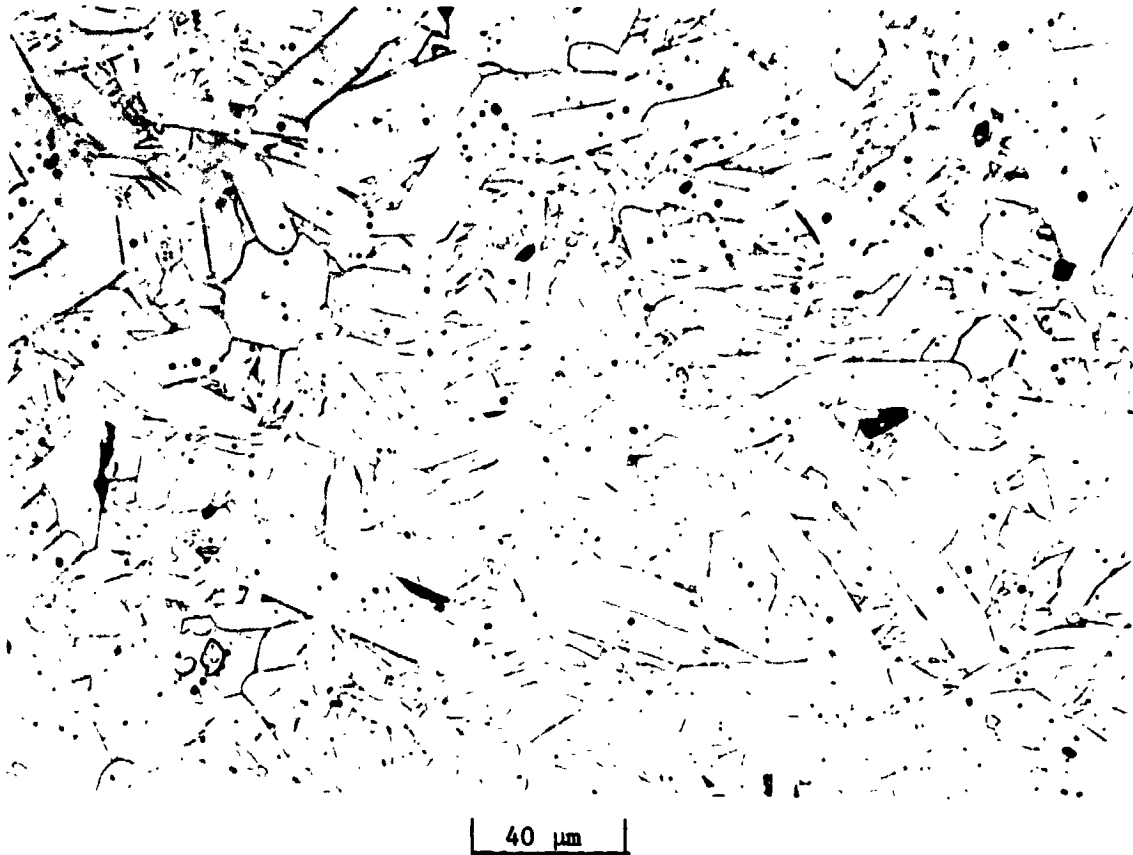


Fig. 2. Typical etched sample of hot-pressed Al_2O_3 -Cr material showing relatively large-grain duplex microstructure. Bright spots within grains are particles of dispersed metal.

Because the duplex structure was found to play a major role in the toughening behavior, an attempt was made to fabricate a duplex structure with a smaller average grain size. This was done by using two-thirds Baikowski CR-10 powder and one-third Alcoa A-17 powder and processing under conditions similar to those used for the previous samples (Table 4). However, the resulting microstructure was not duplex, as shown in Fig. 4.

An attempt was also made to fabricate an Al_2O_3 sample containing no metal but having the large-grain duplex microstructure (DMT-9). The sample did achieve full density and some grain growth occurred. However, it did not develop a duplex grain structure like that observed with the Al_2O_3 -Cr materials (Fig. 5).

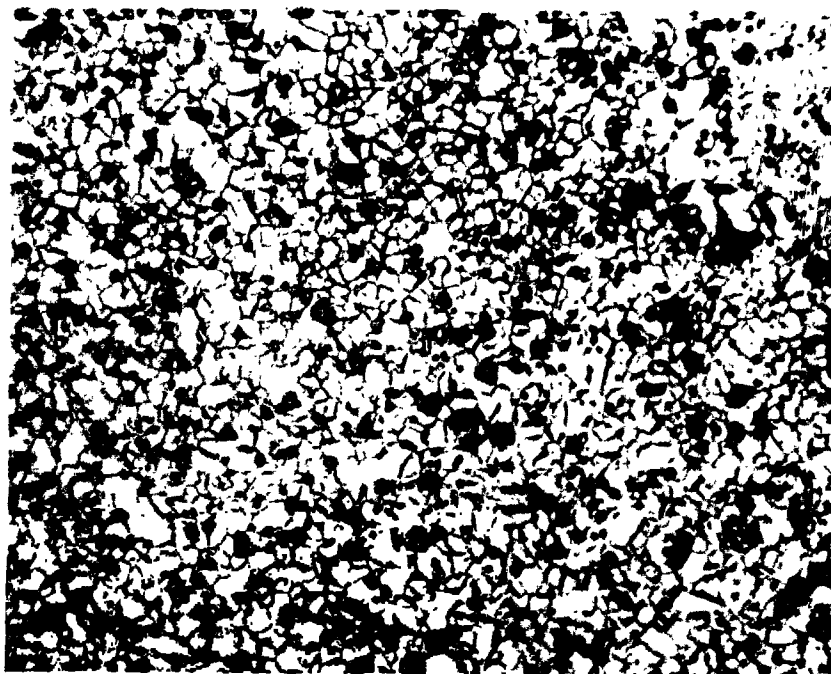


Fig. 3. Etched sample of hot-pressed Al_2O_3 -Cr material made with fine-grain starting powder, showing formation of small equiaxed grains.

Table 4. Summary of results on mechanical testing of DMT alumina

Sample identifi- cation	Composition	Fracture toughness, K_{IC}^a ($\text{MPa}\cdot\text{m}^{1/2}$)	Flexural Strength ^b (MPa)			Average grain size (μm)	Grain morphology	Critical flaw size (μm)
			Room temperature	800°C	1000°C			
AC-4	Al_2O_3 -8 vol % Cr	5.7				6.5	Duplex	
AC-5	Al_2O_3 -2 vol % Cr	6.2				7.5	Duplex	
AC-11	Al_2O_3 -1 vol % Cr	6.8	190	90		15	Duplex	
AC-12	Al_2O_3 -2 vol % Cr	7.8	150	110		14	Duplex	820
AC-13	Al_2O_3 -4 vol % Cr	7.1	240	100	100	10	Duplex	560
AC-14	Al_2O_3 -8 vol % Cr	7.2	200	100		10	Duplex	830
DMT-4	Al_2O_3 -2 vol % Cr	5.8				5.7	Equiaxed	
DMT-5	Al_2O_3 -2 vol % Cr	5.3				5.5	Equiaxed	
AN-1	Al_2O_3 -1 vol % Ni	5.5				5.2	Equiaxed	
AP-1	Al_2O_3 -5 vol % Pt	4.2						
CR-10-19	Al_2O_3 -2 vol % Cr	4.4				5.1	Equiaxed	
CR-10-21	Al_2O_3 -5 vol % Cr	4.5				2.5	Equiaxed	
CR-10-13	Al_2O_3 -1 vol % Cr	4.5				4.7	Equiaxed	
AC-1	Al_2O_3 -2 wt % Cr_2O_3	7.5	200	160	110	10	Duplex	900
AC-2	Al_2O_3 -8 wt % Cr_2O_3	7.3				12	Duplex	
AC-3	Al_2O_3 -2 wt % Cr_2O_3	7.7	220	140	150	11	Duplex	780
Cr-K-13 ^c	Al_2O_3 -1 vol % Cr	6.7						
AC-11 (aged) ^d	Al_2O_3 -1 vol % Cr	6.8						
AC-13 (aged) ^d	Al_2O_3 -4 vol % Cr	6.8						
DMT-9	Al_2O_3	6.7				6.4		

^aUsing applied moment double cantilever beam (AMDCB) technique at room temperature.

^bUsing four-point bend test.

^cThermally aged 1000 h at 1000°C in air. Similar unaged samples had $K_{IC} = 7.0 \text{ MPa}\cdot\text{m}^{1/2}$.

^dThermally aged 2300 h at 1000°C in air.

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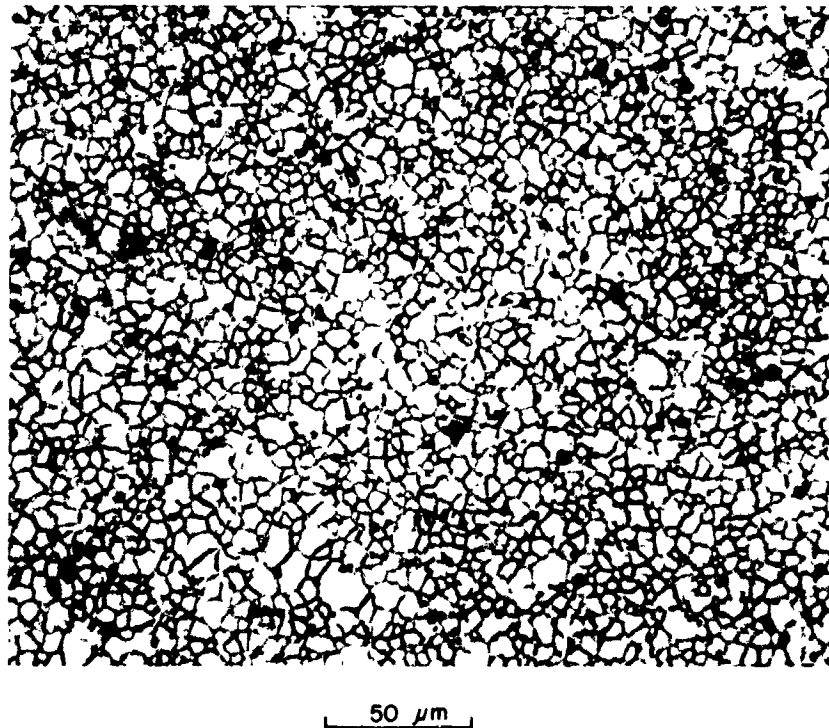


Fig. 4. Etched sample of hot-pressed Al_2O_3 -Cr material made with combination of fine- and coarse-grained starting powders, showing formation of equiaxed grains.

An Al_2O_3 -1 vol % Ni sample did show some development of a duplex grain microstructure (Fig. 6), and some of the grains were quite large ($\sim 100 \mu\text{m}$). However, the nickel acts as a grain growth inhibitor in Al_2O_3 , so the average grain size was relatively small ($\sim 5 \mu\text{m}$ in diam) compared with that of Al_2O_3 -Cr samples fabricated in a similar fashion. As shown later, this type of microstructure had a large effect on the mechanical properties of the Al_2O_3 -Ni material.

MECHANICAL TESTING

Hot-pressed samples of the DMT aluminas were machined with diamond-coated abrasive wheels into specimens for flexural strength and fracture toughness determinations. The flexural strength was determined by the

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Fig. 5. Etched sample of hot-pressed Al₂O₃-Ni. Some grain growth had occurred, but a duplex grain like that in the Al₂O₃-Cr materials did not develop.

four-point bend technique, and the fracture toughness measurements employed the applied moment double cantilever beam (AMDCB) technique. Fracture strengths were determined at room temperature, 800°C, and 1000°C for selected specimens. The fracture toughness measurements were made on nearly all specimens, but only at room temperature. Table 4 summarizes the mechanical testing results.

As shown, the fracture toughness measurements varied from 5 to 8 MPa·m^{1/2} for the Al₂O₃-Cr materials, with the highest value for the 2 vol % Cr sample. No apparent correlation with metal content was observed; however, all the samples with good fracture toughness had the relatively large-grain duplex structure.

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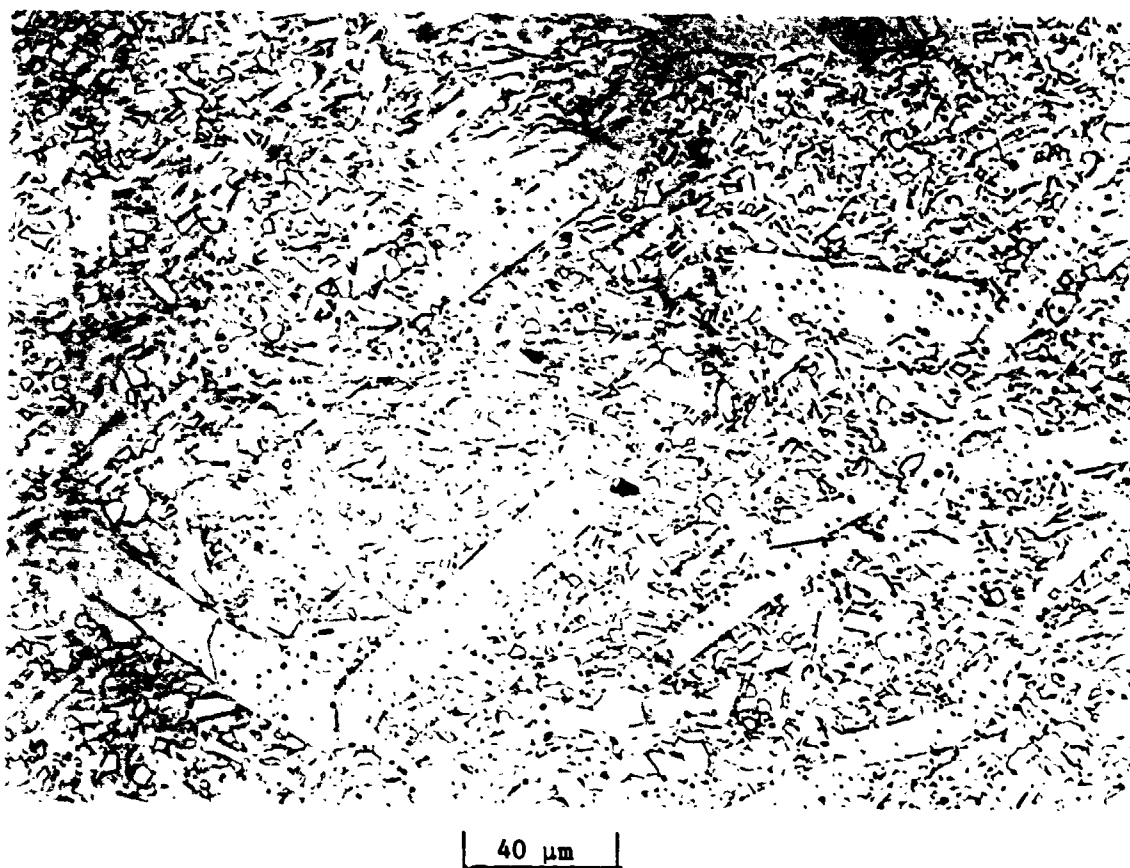


Fig. 6. Etched sample of hot-pressed Al_2O_3 -Ni showing some development of duplex grain structure.

The average grain sizes of the specimens were determined, and correlation with the fracture toughness was evident. This relationship is illustrated in Fig. 7, which includes the measurements for the Al_2O_3 -Ni, Al_2O_3 - Cr_2O_3 , and Al_2O_3 materials. Note that there is no apparent effect of either the volume or type of dispersed metal. As long as the average grain size was similar, the fracture toughness values were similar. Apparently a propagating crack is deflected around the large grains, enhancing the fracture toughness.

The flexural strength measurements were all performed on specimens with relatively large grain sizes ($>10\text{ }\mu\text{m}$ average grain size); consequently, moderate strengths were observed. While the large-grain

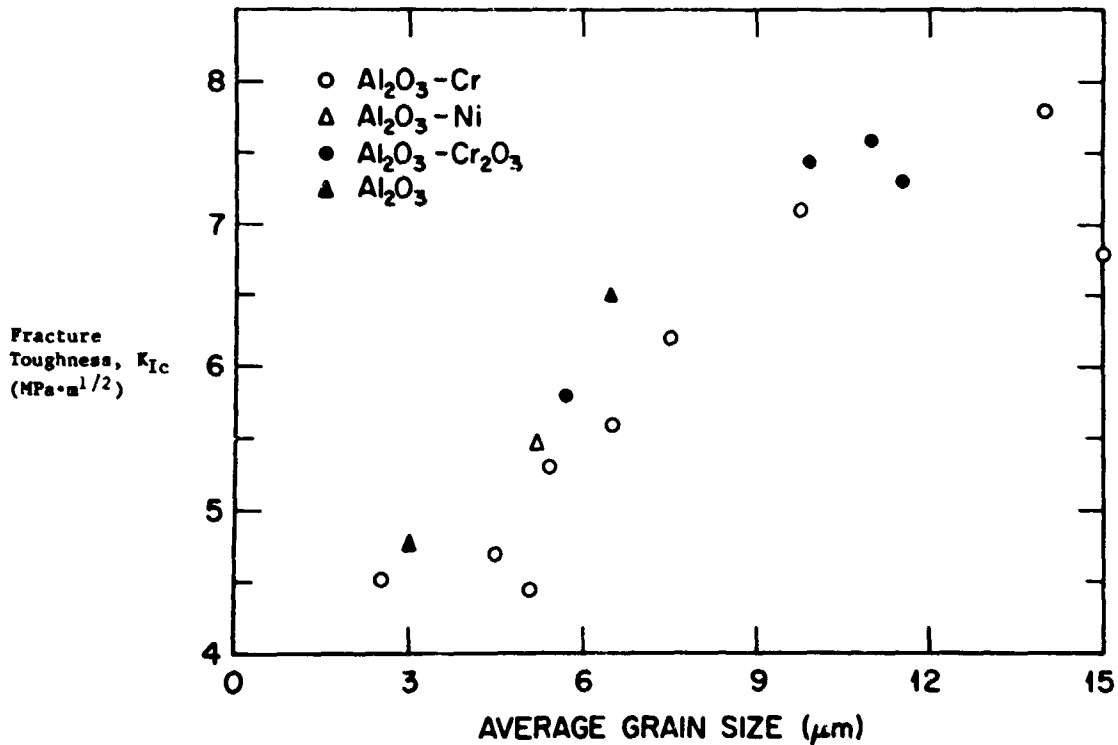


Fig. 7. Fracture toughness is a function of grain size and is independent of the type or volume of dispersed metal.

duplex microstructure enhances the fracture toughness, it is detrimental to the fracture strength. The larger grains can act as critical flaws, whose size reduces the strength significantly. The relationship between tensile fracture strength (σ_f), critical flaw size (c), and fracture toughness (K_{IC}) is given by:

$$\sigma_f = Y K_{IC} c^{-1/2} ,$$

where Y is a geometric factor. Assuming that Y has a value of 0.8 (typical for a semicircular flaw in flexure), the critical flaw size ranges from 560 μm to 1730 μm for the $\text{Al}_2\text{O}_3\text{-Cr}$ materials that had the

large-grain duplex microstructures (Table 4). The flaw sizes for the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions with the duplex microstructures were in the same range. Again, good fracture toughness values are a result of the relatively large duplex grain structure in these materials. Finer grained $\text{Al}_2\text{O}_3\text{-Cr}$ materials have been shown to have greater fracture strengths than those with the duplex grain morphology.⁴

Specimens of selected compositions were thermally aged for long periods (>1000 h) at elevated temperatures (>1000°C) to assess the effect of oxidation on the fracture toughness. As shown in Table 4, very little change in the fracture toughness is observed after thermal aging. The same effect was observed in a previous study⁴ and is shown in Fig. 8. In that study, some of the samples exposed at 1150°C had turned pinkish in

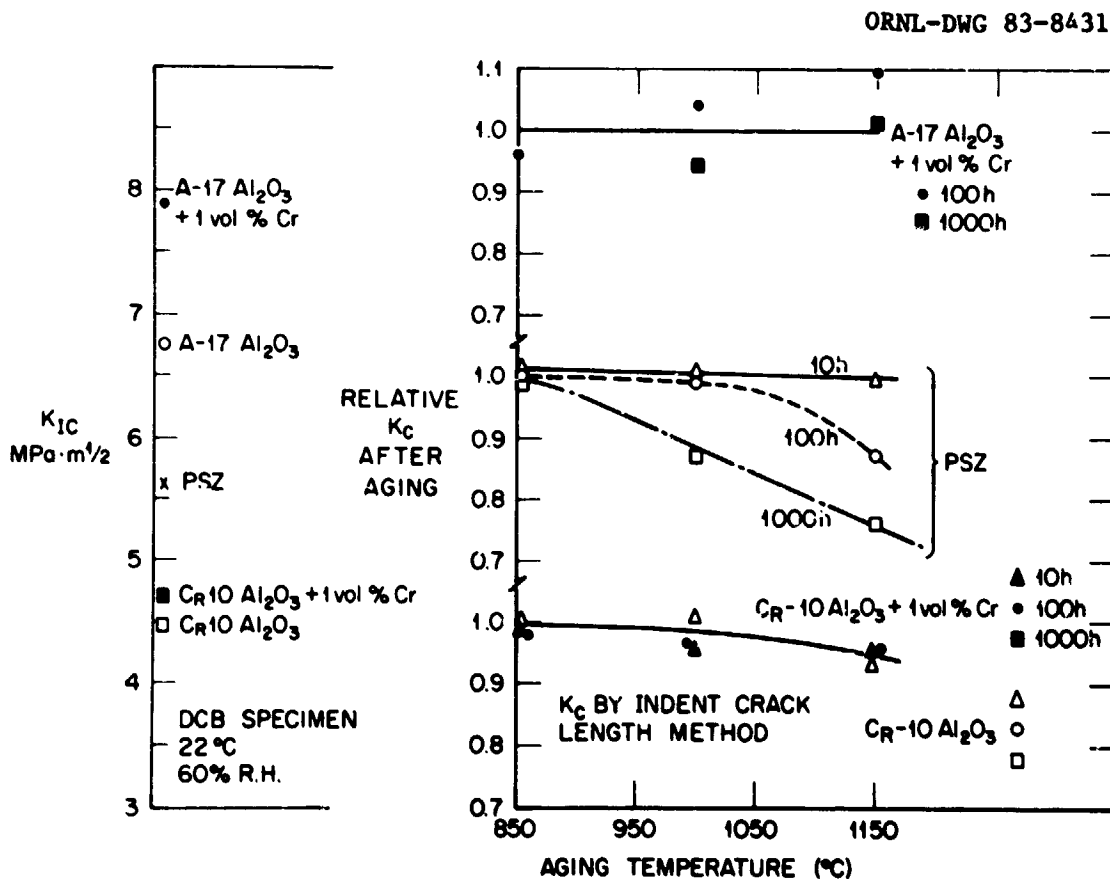


Fig. 8. Critical fracture toughness can be affected by aging at elevated temperatures.

color (indicating oxidation of the Cr and solid solution formation), but their fracture toughness had not changed appreciably. We speculate that the grain sizes changed little at the exposure temperatures and, consequently, the fracture toughness changed very little.

PRESSURELESS SINTERING

Although hot pressing of the DMT alumina produces dense materials, the ability to pressureless sinter the composite is desirable for fabrication of components. Hot pressing provides specimens with relatively simple shapes, whereas pressureless sintering can provide more complex and near-net-shape pieces.

In our first attempts to sinter the Al_2O_3 -Cr materials, we used the same powders as employed in the hot-pressing fabrication study. The results of those efforts are summarized in Table 5. As shown, the powders containing Alcoa A-17 Al_2O_3 required sintering aids (e.g., MgO) and high temperatures (1800°C) to achieve $>90\%$ of theoretical density (TD). However, weight loss due to Cr volatilization was a problem. Removing the residual carbon in the powder by heat treating at 550°C in air also did not improve the sinterability of the Al_2O_3 -Cr material.

Table 5. Summary of results on pressureless sintering of DMT alumina

Sample identifi- cation	Composition	Sintering Conditions		Density	Weight loss (%)
		Temperature ($^\circ\text{C}$)	Time (h)	(% TD)	
ACC-7	Al_2O_3 -1 vol % Cr ^a	1750	1/2	84-85	
ACC-7	Al_2O_3 -1 vol % Cr ^{a,b}	1550	2	65-66	
AC-11	Al_2O_3 -1 vol % Cr ^{a,c}	1800	1	92-93	1.7
	Al_2O_3 ^d	1500	1	91	
DMT-4	Al_2O_3 -2 vol % Cr ^{a,d}	1600	1/2	80-82	0.4
DMT-5	Al_2O_3 -2 vol % Cr ^{a,e}	1600	1/2	91-94	0.8
DMT-6	Al_2O_3 -4 wt % Cr ₂ O ₃ ^{a,e}	1550	1/2	95	0.6

^aMade with Alcoa A-17 alumina.

^bHeat treated at 550°C for 20 h in air to remove any residual carbon.

^cUsed 0.5 wt % MgO as a sintering aid.

^dMade with 2/3 Baikowski CR-10 plus 1/3 Alcoa A-17.

^eMade with Baikowski CR-10 alumina.

A typical microstructure for the sintered materials made with Alcoa A-17 Al_2O_3 is shown in Fig. 9. The starting Al_2O_3 grain size is $\sim 5 \mu\text{m}$, and grain size in the sintered material is $\sim 8 \mu\text{m}$. As shown, no excessive grain growth has occurred and the microstructure bears little resemblance to the large grain duplex structure typical of the hot-pressed materials.

It is well known that powders with small particulate size are easier to sinter than those with a coarse particulate size. We sintered some Al_2O_3 -Cr materials made with Baikowski CR-10 Al_2O_3 , which had an average initial particle size on the order of $0.2 \mu\text{m}$. As shown in Table 5, those materials were sintered to $>90\%$ TD at temperatures $<1600^\circ\text{C}$ with relatively low weight losses. The microstructure consisted of equiaxed grains with

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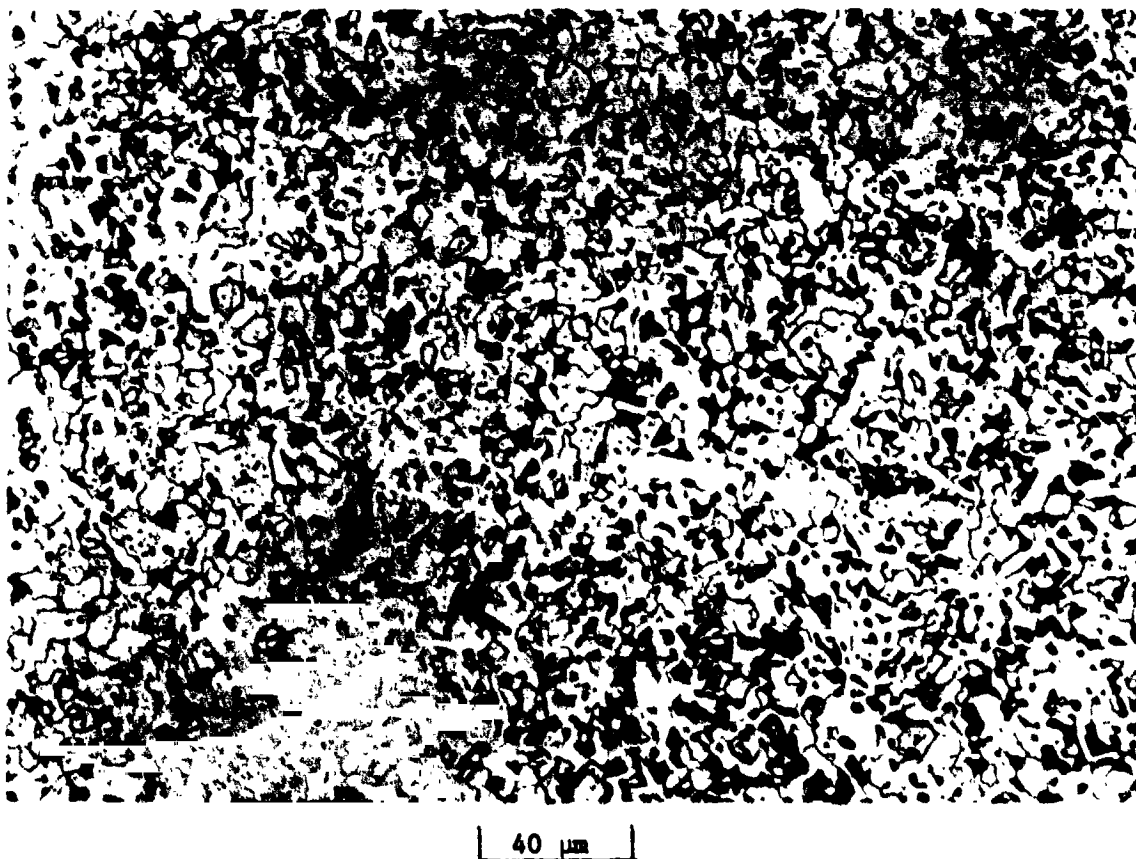


Fig. 9. Etched sample of Al_2O_3 -Cr material, made with Alcoa A-17 Al_2O_3 fabricated by pressureless sintering.

an average size of $\sim 3 \mu\text{m}$. The $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution also sintered easily. The sample made of the combination of Baikowski CR-10 and Alcoa A-17 Al_2O_3 did not sinter as easily as the other powders made entirely from Baikowski CR-10. The difference is directly attributable to the relatively coarse Alcoa A-17 Al_2O_3 fraction.

THERMAL CONDUCTIVITY

Along with the mechanical properties and chemical stability of the DMT aluminas, the thermal properties are also of concern for uncooled diesel engine applications where low thermal conductivity is desirable. The thermal conductivity of an $\text{Al}_2\text{O}_3\text{-1 vol } \%$ Cr sample was calculated from heat capacity and laser flash diffusivity measurements.* Those results are summarized in Table 6. For comparison the thermal conductivity for a commercial partially stabilized zirconia (PSZ) calculated in the same fashion is shown, and also values for Al_2O_3 and $\text{Al}_2\text{O}_3\text{-4 wt } \%$ Cr_2O_3 .

At room temperature (23°C) the thermal conductivity of the $\text{Al}_2\text{O}_3\text{-1 vol } \%$ Cr material is almost six times higher than that of the PSZ, but it decreases to about three times higher at a typical uncooled diesel combustion chamber temperature of 1000°C . The thermal conductivity of the $\text{Al}_2\text{O}_3\text{-Cr}$ material is almost 36% less than that of the pure Al_2O_3 at 100°C . However, above $\sim 500^\circ\text{C}$, the conductivities are essentially the same. Solid solutions of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ have been reported to have lower thermal conductivity than pure Al_2O_3 because of greater thermal scattering.⁶ X-ray analysis of $\text{Al}_2\text{O}_3\text{-Cr}$ samples has always shown that some of the Cr is in solid solution with the Al_2O_3 even when a carbon source is used to reduce the Cr_2O_3 . Evidently even a small amount of Cr in solid solution is enough to reduce the thermal conductivity significantly, but the reduction occurs at relatively low temperatures, i.e., $< 500^\circ\text{C}$.

*Measurements made at Purdue University.

Table 6. Summary of thermal conductivity calculations

Temp. (°C)	Al ₂ O ₃ -1 vol % Cr ^a			PSZ ^{a,b}	Al ₂ O ₃ ^c
	Specific Heat (W·s·gm ⁻¹ ·K ⁻¹)	Diffusivity (cm ² ·s ⁻¹)	Conductivity (W·cm ⁻¹ ·K ⁻¹)	Conductivity (W·cm ⁻¹ ·K ⁻¹)	Conductivity (W·cm ⁻¹ ·K ⁻¹)
23	0.747	0.0695	0.205	0.0354	
100	0.894	0.0527	0.186	0.0352	0.289
200	1.003	0.0395	0.156	0.0327	0.218
300	1.076	0.0322	0.137	0.0307	0.168
400	1.124	0.0270	0.120	0.0293	0.134
500	1.155	0.0237	0.108	0.0284	0.112
600	1.173	0.0206	0.0953	0.0270	0.095
700	1.193	0.0187	0.0880	0.0257	0.086
800	1.211	0.0159	0.0760	0.0244	0.078
900	1.228	0.0155	0.0751	0.0232	0.072
1000	1.242	0.0143	0.0701	0.0222	

^aDetermined by heat capacity and laser flash diffusivity measurements at Purdue University.

^bPSZ: partially stabilized zirconia.

^cSource: W. D. Kingery, *Introduction to Ceramics*, Chap. 14, John Wiley and Sons, Inc., New York, 1960.

DISPERSED-METAL TOUGHENING OF ZIRCONIA

As part of the work plan for this project, the use of finely dispersed metal particles to toughen partially stabilized zirconia (PSZ) was investigated. However, the effort was limited because of Al₂O₃-Cr results showing the importance of microstructure to the fracture toughness. In addition, dispersion of metals in PSZ is very difficult compared with dispersion in alumina because the high oxygen ion mobility in the zirconia at high temperature favors oxidation of the metal.

The original plan was to hot press a series of PSZ metal compositions and determine mechanical properties, including fracture strength and toughness. A sample containing 1 vol % Cr was prepared by using a synthesis route similar to that used for the Al₂O₃-Cr materials. PSZ powder was mixed with chromium nitrate and paraffin and fired in a hydrogen atmosphere to 1150°C. This powder was subsequently hot pressed

at 1600°C and 41 MPa. Upon removal from the graphite die the sample was found to be cracked extensively, and it broke into numerous pieces.

Evidently during cooling from elevated temperature in the hot press, the tetragonal to monoclinic phase transformation occurred and resulted in a volume expansion and cracking of the sample. The pressure in the hot press had been maintained during cooling; however, the cooling rate was slow enough to favor the transformation. PSZ ceramics are normally fabricated by quenching through the transformation temperature to retain the tetragonal phase. In addition, there may have been an effect of the dispersed metal particles and/or any excess carbon on the phase transformation. Those possible effects were not studied in detail.

Because results for Al_2O_3 -Cr materials showed that the microstructure and not the dispersed metal particles had the greatest influence on the fracture toughness, we believed that DMT-PSZ would have little chance for improvement over normal PSZ ceramics. In addition, because the initial sample fabrication evidenced problems, it was apparent that fabrication of appropriate samples for mechanical testing of the DMT-PSZ would have required a substantial development effort, which was not justified. Therefore, we decided to concentrate our efforts on understanding the Al_2O_3 -Cr materials.

CONCLUSIONS

The Al_2O_3 -Cr materials fabricated by hot pressing showed good fracture toughness for ceramic materials ($<8 \text{ MPa}\cdot\text{m}^{1/2}$), which is about double that of fine-grained pure alumina. Consequently, their thermal shock resistance is good. However, their fracture strengths were relatively low — on the order of 190 to 240 MPa vs 350 to 580 MPa for pure alumina. The good fracture toughness was found to be related to the relatively large-grain duplex structure of the hot-pressed materials. This structure was the result of a combination of the metallic additives and the hot pressing technique as it was not found in samples that were hot pressed without the metal or in those containing metal that were pressureless sintered. When the grain size was reduced by using

fine-grained Al_2O_3 starting powder and a lower hot-pressing pressure, the fracture toughness decreased. Specimens made by pressureless sintering also did not develop a duplex grain structure and had low toughness. Thus, the hot-pressed Al_2O_3 -Cr materials with the duplex grain structure have application in areas where thermal shock resistance and high toughness are necessary but where high strength is not a requirement.

The fracture toughness of Al_2O_3 with dispersions of Ni and Pt was found to be inferior to that of the Al_2O_3 -Cr materials. Nickel acts as a grain growth in alumina and, although some duplex grain structure is developed, the average grain size is still relatively small (in comparison with that of the Al_2O_3 -Cr materials). Consequently, the fracture toughness is not greatly enhanced. The Pt-containing materials produced a relatively large-grain duplex structure, but the fracture toughness was not enhanced as much as it was when Cr was the dispersed metal. We speculate that the bond strength between the Pt and the Al_2O_3 is so low that the fracture strength and toughness are low.

The hot-pressed Al_2O_3 - Cr_2O_3 materials also showed good fracture toughness values in the range of 7.3 to 7.7 $\text{MPa}\cdot\text{m}^{1/2}$. As with the Al_2O_3 -Cr samples, this toughness is due to the large-grained duplex microstructure. In addition, the fracture strengths of these materials were slightly higher than those of the Al_2O_3 -Cr samples with comparable toughness values, indicating some possible strengthening due to solid-solution hardening.

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